Cyclization of 32 with 2.0 Equiv of Me_2AlCl. Me_2AlCl (2.28 mL of a 1.14 M solution, 2.6 mmol, 2 equiv) was added to a solution of **32** (250 mg, 1.3 mmol) in 5 mL of CH_2Cl_2. This solution was stirred at 0 °C for 1 h. Normal workup gave 250 mg of crude material. Purification of 210 mg on silica gel (2:1 pentane–ether) gave 120 mg (58%) of **36**.

Cyclization of 38. Addition of $EtAlCl_2$ (0.3 mL of a 1.53 M solution in heptane, 0.45 mmol) to a solution of enone **38** (100 mg, 0.45 mmol) in 3 mL of CH_2Cl_2 at 25 °C. The reaction was stirred 1.5 h at 25 °C. TLC showed no reaction had occurred so an additional 0.15 mL of $EtAlCl_2$ solution was added. The reaction was complete in 10 min. Normal workup gave 97.3 mg of **40** as a 1:1 mixture of isomers which was chromatographically pure: NMR ($CDCl_3$) δ 5.91 (br s, 1), 2.5–1.8 (m, 4) 1.90 (br s, 3), 1.24 (br, 12), 0.93 (d, 0.5 × 3, $J = 7$ Hz), 0.80 (br t, 3, $J = 6$ Hz), 0.69 (d, 0.5 × d, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) δ 199.3, 164.7, 164.5, 128.6, 128.4, 45.5, 43.2, 36.2, 36.0, 35.0, 33.7, 33.2, 32.3, 31.7, 31.4, 29.4, 29.3, 27.9, 27.5, 23.0, 22.6, 22.5, 21.4, 18.2, 15.1, 13.9; IR (neat) 1670, 1618 cm^{-1}.

To ensure that isomerization of **40** had not occurred after cyclization, **38** (50 mg, 0.22 mmol) in 1.5 mL of $EtAlCl_2$ was treated with $EtAlCl_2$ (0.30 mL of a 1.53 M solution in heptane, 0.45 mmol, 2 equiv) at −78 °C. The reaction mixture was stirred for 5 h at −78 °C and quenched to give 49 mg (99%) of a 1:1 mixture of recovered **38** and **40**. NMR analysis indicated that **40** was present as a 1:1 mixture of isomers.

Acknowledgment. We thank the Research Corp., the National Institutes of Health, and the Mobile Foundation for financial support. A Halcon fellowship to D.J.R. is gratefully acknowledged. The synthesis and cyclization of **38** was carried out by Thomas C. Kirk. We thank Bedoukian Research Inc. for generous gifts of chemicals.

Registry No. 3, 106-72-9; **4a**, 66575-33-5; **4b**, 66575-34-6; **5a**, 83026-65-7; **5b**, 83059-39-6; **7a**, 81980-08-7; **8a**, 83059-40-9; **8b**, 83059-41-0; **9a**, 25073-02-3; **10a**, 81980-09-8; **11a**, 82009-61-8; **12**, 106-23-0; **14**, 3664-64-0; **14** (dimer), 83026-79-3; **15a**, 76156-38-2; **15b**, 76189-17-8; **16**, 504-37-0; **17**, 76123-37-0; **18**, 2277-19-2; **19**, 2277-20-5; **20**, 76123-38-1; **21**, 76156-39-3; **22**, 76156-40-6; (*E*)-**23**, 83026-66-8; (*Z*)-**23**, 81980-06-5; **24**, 41547-22-2; **25**, 83026-67-9; **26**, 79925-78-3; **27**, 83059-42-1; **28**, 4423-94-3; **29**, 1193-70-0; **30**, 83026-68-0; **31**, 83026-69-1; **32**, 19870-49-6; **33**, 83026-70-4; **34**, 83026-71-5; **35**, 83026-72-6; **36**, 83026-73-7; **37**, 83026-74-8; **38**, 83026-75-9; **40** (isomer 1), 83026-76-0; **40** (isomer 2), 83026-77-1; 3,7,7-trimethyl-2-octanone, 83026-78-2; Me_2AlCl, 1184-58-3; $MeAlCl_2$, 917-65-7; $EtAlCl_2$, 563-43-9.

Conformational Dependence in the Mass Spectrum of Cyclohexanecarboxaldehyde

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The mass spectrum of cyclohexanecarboxaldehyde (1) was shown to fit a composite of the mass spectra of the equatorial and axial conformers. By comparison of the fragmentation processes from $1^{+\cdot}$ with the processes from the fixed conformers corresponding to $1^{+\cdot}$, the processes involving hydrogen abstraction by the oxygen atom as the initial step were attributed to the axial conformer, and the processes involving initial ring bond cleavage were attributed to the equatorial conformer. The abundant α-cleavage ion at 50 eV was attributed to both conformers, analogous to its occurrence in the fixed conformers. The loss of C_2H_4O from $1^{+\cdot}$ was found to be loss of CH_3CHO and thus was attributed to equatorial $1^{+\cdot}$. Initial hydrogen abstraction in axial $1^{+\cdot}$ was found to occur at a faster rate than initial ring bond stretching, whereas in equatorial $1^{+\cdot}$ initial ring bond stretching was found to occur at a faster rate than conversion to axial $1^{+\cdot}$.

The McLafferty rearrangement in the molecular ions of nonfixed conformers of cyclohexyl acetate and diethyl cyclohexylmalonates was found to occur from the two chair forms in the same proportion as that in which the two chair forms existed before ionization, on the basis of the known stereoselectivity of the fixed conformers.[1] The γ-hydrogen abstraction process was proposed to be faster than chair-to-chair interconversion.[1] The McLafferty rearrangement from both chair forms would be expected to be of very low activation energy, similar to the McLafferty rearrangement in the propyl acetates, where the experimental and calculated appearance energies were equal to the ionization energy.[2] There was no need for internal excitation of the molecular ion, in agreement with the extremely low relative abundance of the molecular ion.[2] In contrast, an activation energy would be expected for the chair-to-chair interconversion in the molecular ions of the cyclohexyl acetates and corresponding cyclohexylmalonates.[3]

In this study of the fragmentation processes of the molecular ion of cyclohexanecarboxaldehyde (1), only the axial conformer has the required geometry for hydrogen abstraction in a six-membered transition state, and further rearrangement is required for fragmentation. However, by comparison to the mass spectra of analogous fixed conformers and cyclohexane, the fragmentation processes of $1^{+\cdot}$ were found to be consistent with a dependence on the initial stereochemistry of the aldehyde.

Results

In Table I are given data on the primary product ions and neutral fragments from $1^{+\cdot}$. The empirical structures of the product ions were confirmed by high-resolution mass spectroscopy. For the estimation of product ion energy levels, with various structures for the ions and neutral

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(1) Rej, R. N.; Bacon, E.; Eadon, G. *J. Am. Chem. Soc.* **1979**, *101*, 1668.

(2) Benoit, F. N.; Harrison, A. G.; Lossing, F. P. *Org. Mass Spectrom.* **1977**, *12*, 78.

(3) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965.

0022-3263/82/1947-4545$01.25/0

Table I. Calculated and Experimental Energy Levels of the Fragment Ions of $1^{+\cdot}$

m/z	RA[a]	neutral fragment A	ΔH_f of A[b]	B[c]	ΔH_f of B[b,d]	IE of B[e]	calcd *E*[f]	exptl *E*[g]	AE[h] of B
112	28			$c\text{-}C_6H_{11}CHO$	−56.2	9.6[h]		165	
94	31	H_2O	−57.8	$\overline{CH_2CH_2CH_2CH{=}CHC}{=}CH_2$	19.0	8.4[i]	154	168	9.7
		H_2O	−57.8	$CH_2{=}CH(CH{=}CH)_2CH_3$	31.8	8.1[j]	156		
81	13	$HOCH_2\cdot$	−6.1	$\overline{CH_2CH_2CH_2\dot{C}HCH{=}CH}$	30.0	6.7[k]	178	184	10.4
		$HOCH_2\cdot$	−6.1	$CH_2{=}CH\dot{C}HCH{=}CHCH_3$	40.4	6.7[l]	188		
80	2	CH_3OH	−48.0	$\overline{CH_2(CH{=}CH)_2CH_2}$	25.9	8.25	168		*m*
71	9	$CH_2{=}CHCH_2\cdot$	39.1	$CH_3CH{=}CH\dot{C}HOH$	−8.4	6.3[b]	176	175	10.0
		$CH_2{=}CHCH_2\cdot$	39.1	$c\text{-}C_3H_5\dot{C}HOH$	9.4	6.4[n]	196		
		$CH_2{=}CHCH_2\cdot$	39.1	$CH_3CH_2\dot{C}HCHO$	−11.4	7.55[o]	201		
45	3	$CH_2{=}CH\dot{C}HCH{=}CH_2$	48.3	$CH_3\dot{C}HOH$	−16.6	6.6[q]	183	184	10.4
70	28	$CH_2{=}CHCH_3$	4.9	$CH_2{=}CHCH{=}CHOH$	−17.7	8.4[r]	180	180	10.2
		$CH_2{=}CHCH_3$	4.9	$CH_3CH{=}CHCHO$	−26.6	9.73	202		
68	41	CH_3CHO	−39.7	$CH_3CH{=}CHCH{=}CH_2$	18.3	8.56	175	174	10.0
		$CH_2{=}CHOH$	−31.3	$CH_3CH{=}CHCH{=}CH_2$	18.3	8.56	184		
84	6	$CH_2{=}CH_2$	12.5	$\overline{CH_2CH_2CH_2CH{=}CHO}$	−29.9	8.34	175		*m*
		$CH_2{=}CH_2$	12.5	$CH_3CH{=}CHCH_2CHO$	−25.8	9.3[s]	201		
56	10	$CH_2{=}CHCHO$	−18.8	$CH_3CH{=}CHCH_3$	−2.7	9.1	188	186	10.5
97	5	$CH_3\cdot$	34.9	$CH_3(CH{=}CH)_2\dot{C}HOH$	5.2	5.9[t]	176	174	10.0
		$CH_3\cdot$	34.9	$CH_3CH{=}CH\dot{C}(OH)CH{=}CH_2$	0.9	6.2[u]	178		
		$CH_3\cdot$	34.9	$\overline{CH_2CH_2CH{=}CH\dot{C}(OH)CH_2}$	−12.3	6.0[v]	161		
		$CH_3\cdot$	34.9	$CH_2{=}C(CHO)\dot{C}(CH_3)_2$	−10.7	6.9[w]	183		
57	14	$CH_2{=}CH\dot{C}HCH_3$	30.3	$CH_2{=}CH\dot{C}HOH$	−0.6	6.6[b]	182	183	10.4
		$CH_2{=}CH\dot{C}HCH_3$	30.3	$CH_3\dot{C}HCHO$	−6.4	7.65[p]	200		
		$CH_2{=}CHCH_2CH_2\cdot$	46.8	$CH_2{=}CH\dot{C}HOH$	−0.6	6.6[b]	198		
82	4	H_2CO	−26.0	$c\text{-}C_6H_{10}$	−0.8	8.95	179	183	10.4
83	68	$H\dot{C}{=}O$	9.0	$c\text{-}C_6H_{11}\cdot$	13.7	6.85[b]	180	183	10.4
	3	$CH_3CH_2\cdot$	26.5	$CH_2{=}CHCH{=}CH\dot{C}HOH$	13.0	6.1[x]	180		
111	1	$H\cdot$	52.1	$c\text{-}C_6H_{11}\dot{C}{=}O$	−21.3	6.5[y]	180		*m*

[a] Relative abundance (RA) at 50 eV corrected for isotope abundance. See Experimental Section for the RA of other ions. [b] See Appendix for detail; in kcal/mol. [c] Fragment which carries the charge. [d] Not ionized. [e] Reference 56 unless otherwise noted; in eV. [f] $\Delta H_f{}^{\circ}{}_{(q,298)}$ (A) + $\Delta H_{f(g,298)}{}^{\circ}$ (B) + IE(B); kcal/mol. [g] AE (this work) + $\Delta H_f{}^{\circ}{}_{(q,298)}$ (1); in kcal/mol. The ΔH_f of the axial form of 1 is −55.2 kcal/mol.[41] [h] This work; in eV. [i] Estimated to be 0.1 eV less than the IE of 2-methyl-1,3-pentadiene (Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 189). [j] Reference 37. [k] Estimated to be 0.1 eV less than the IE of 2-cyclopenten-1-yl.[b] The IE of cyclohexyl is 0.1 eV less than the IE of cyclopentyl.[b] [l] Estimated to be 0.35 eV less than the IE for $CH_2{=}CH\dot{C}HCH{=}CH_2$.[b] The IE of $CH_3\dot{C}HCH{=}CHCH_3$[b] is 0.35 eV less than the IE of $CH_3\dot{C}HCH{=}CH_2$.[17,b] [m] RA too low. [n] Estimated to be the same as the IE of $C_2H_5\dot{C}HOH$.[17,b] [o] Estimated to be 0.1 eV less than the IE of $CH_3\dot{C}HCHO$.[p] [p] Estimated to be higher than the IE of $CH_3\dot{C}HCH_3$[b] by the amount (0.4 eV) that the IE of propenal is higher than the IE of propene.[e] [q] See ref 17 and Appendix. [r] Estimated to be 0.2 eV less than the IE of 1,3-pentadiene[e] and 0.4 eV more than the IE of 1-methoxy-1,3-butadiene, 8.0 eV (Sustmann, R.; Schubert, R. *Tetrahedron Lett.* **1972**, 2739), similar to the IE of vinyl alcohol, 9.25 eV,[9b] in relation to the IE of propene, 9.7 eV,[e] and methyl vinyl ether, 8.6 eV (Schore, N. E.; Turro, N. *J. Am. Chem. Soc.* **1975**, *97*, 2482. Trofimov, B. A.; Molder, U.; Pikver, R.; Vyalykh, E. P.; Nedolya, N. A. *Izv. Akad. Nauk SSSR, Ser, Khim.* **1974**, 2731). Also see ref 38 for the estimated ΔH_f of 176 kcal/mol for $H_2C{=}CHCH{=}CHOH^{+\cdot}$. [s] Estimated to be intermediate between the IE of 2-pentene, 8.9 eV (Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973), and pentanal, 9.7 eV.[58] [t] Estimated to be 0.4 eV less than the IE of $CH_3CH{=}CHCHOH$.[b] [u] Estimated to be 0.1 eV less than the IE of $CH_3CH{=}CH\dot{C}HOH$.[b] [v] Estimated to be the same as the IE of 1-hydroxycyclopentyl obtained from the adjusted PA of cyclopentanone.[17,b] [w] Estimated to be the same as the IE of $CH_2{=}CH\dot{C}(CH_3)_2$.[b] [x] Estimated to be 0.2 eV less than the IE of $CH_3CH{=}CH\dot{C}HOH$.[b] [y] Estimated to be 0.1 eV less than the IE of $CH_3CH_2\dot{C}{=}O$.[e]

fragments, experimentally determined ΔH_f's were used, where available. For the others, the additivity procedure[4] was used for the estimation of ΔH_f's of the radicals and neutral components. Ionization energies (IE) of these compounds were estimated from IE's of analogous compounds. Ionization energies of radicals are known to vary little with changes in structure beyond a few atoms from the radical center.[5,6]

Appearance energies (AE) of the fragment ions from $1^{+\cdot}$ were measured by the semilogarithmic method. This method is known to give higher values for AE's than those obtained by photoionization or by energy-resolved mass spectroscopy, the excess amount depending on instrumental conditions.[7] However, when the semilogarithmic curves for two ions are parallel, their AE differences should be semiquantitatively correct.[7a] In this study we used acetone as the internal standard which has a fragment ion

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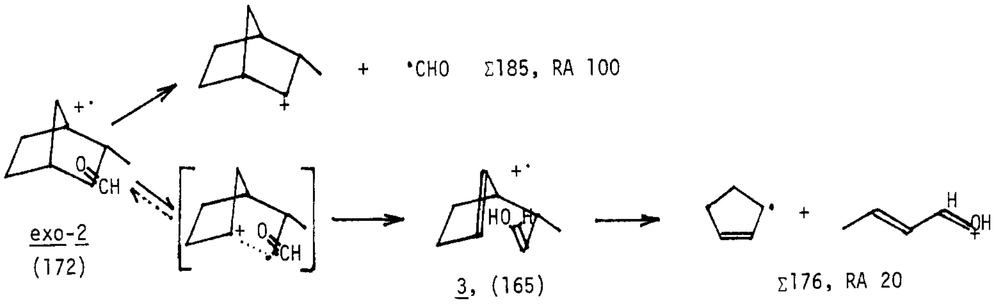
(4) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(5) Lossing, F. P.; Maccoll, A. *Can. J. Chem.* **1976**, *54*, 990.

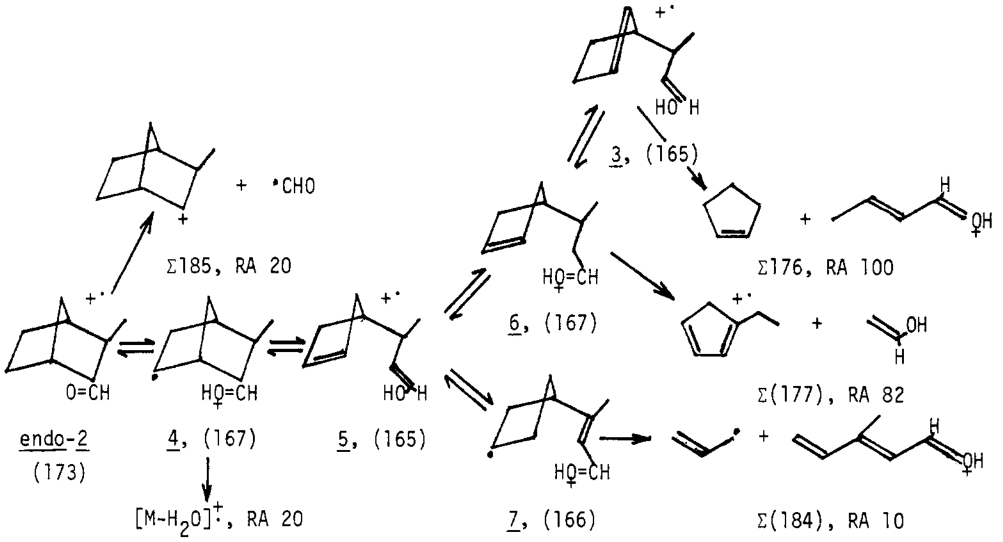
(6) Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9.

(7) For a discussion of the semilog method, see: (a) Morgan, R. P.; Derrick, P. J.; Loudon, A. G. *J. Chem. Soc., Perkin Trans. 2*, **1980**, 306. (b) Baldwin, M. A. *Org. Mass Spectrom.* **1979**, *14*, 601. (c) Rosenstock, H. M. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *20*, 139.

Scheme I



Scheme II



(*m/z* 43) of high intensity and known AE.[8] The internal standard was used to determine the I/I_{50} level at which the AE values for the fragment ions of $1^{+\cdot}$ were measured (see Experimental Section). These AE values are given in Table I.

For simple cleavage reactions, the calculated product-ion energy levels should be similar to the experimental energy levels as calculated from the AE values. For rearrangement reactions the excess energy may be larger, and the reaction may show an appreciable reverse activation energy.[9] The kinetic shift should be small for activation energies (E_0) to ~1 eV.[7b,10]

For a given molecular ion and internal energy, the rate of formation of a fragment ion depends on the E_0 and the frequency factor for that process.[9] At 70 eV, the abundances of the ions reflect the relative frequency factors for the formation of those ions.[9]

It is possible that some fragment ions are formed by more than one mechanism and have different structures with different product-ion energy levels. However, in order for there to be a significant contribution from a higher E_0 process to the abundance of an ion, the frequency factor for that process would have to be higher than for the lower E_0 process.[9]

In the various schemes are given ΔH_f's of ions and calculated energy levels denoted by $\sum$. Estimated ΔH_f's and energy levels are given in parentheses. Estimated ΔH_f's of intermediate and other ions not given in Table I are in the Appendix.

Discussion

Mass Spectra of Fixed Conformers Related to 1. The compounds with fixed conformations which have mass spectra analogous to the mass spectrum of 1 are *exo*- and *endo*-3-methylbicyclo[2.2.1]heptane-2-carboxaldehyde (2).[11] The major process from *exo*-$2^{+\cdot}$ was α cleavage to give the $[M - CHO]^+$ ion.[12] There was a moderate amount

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[8] Average of the values reported by: Murad, E.; Inghram, M. G. *J. Chem. Phys.* **1964**, *40*, 3263. Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1209.

[9] (a) Williams, D. H.; Howe, I. "Principles of Organic Mass Spectrometry"; McGraw-Hill: London, 1972. (b) Bentley, T. W.; Johnstone, R. A. W. *Adv. Phys. Org. Chem.* **1970**, *8*, 151.

[10] Rosenstock, H. M.; McCulloh, K. E.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 327.

[11] Thomas, A. F.; Willhalm, B. *Helv. Chim. Acta* **1967**, *50*, 826.

[12] The ΔH_f of the 2-norbornyl cation as determined from the proton affinity of 2-norbornene[13] indicates that it may be the nonclassical ion. A comparison of its ΔH_f (183.2 ± 2 kcal/mol[13]) with the ΔH_f (167.5 ± 3 kcal/mol[16]) of the classical 2-methyl-2-norbornyl cation[19] relative to the ΔH_f (183.8 ± 1.9 kcal/mol[20]) of the cyclopentyl cation with the ΔH_f (164.2 ± 1.7 kcal/mol[20]) of the 1-methylcyclopentyl cation and relative to the ΔH_f (171 ± 3 kcal/mol[20]) of the cyclohexyl cation with the ΔH_f (152.7 ± 1.7 kcal/mol[20]) of the 1-methylcyclohexyl cation would indicate a stabilization energy of 3-4 kcal/mol for the 2-norbornyl cation. However, there is evidence in ionization reactions of 2-norbornyl compounds that bridging lags behind ionization,[19] similar to the rearrangement of the cyclohexyl cation at lifetimes in excess of 10^{-7} s in the dilute-gas state.[21]

[13] Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1084. Their value was adjusted to a ΔH_f of 162.1 kcal/mol for the *tert*-butyl cation[14] and a ΔH_f of 21.4 kcal/mol for 2-norbornene.[15]

[14] McLoughlin, R. G.; Traeger, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5791.

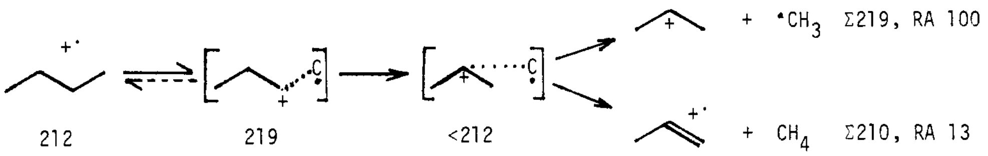
[15] Rogers, D. W.; Choi, L. S.; Girellini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810.

[16] The value reported by Aue and Bowers[17] was adjusted to a ΔH_f of 162.1 kcal/mol for the *tert*-butyl cation[14] and a ΔH_f of 11.2 kcal/mol for 2-methylenenorbornane by additivity,[4] relative to the ΔH_f of −12.42 kcal/mol for norbornane[15] and an additional 1.6 kcal/mol for the exo double bond as in methylenecyclohexane.[18]

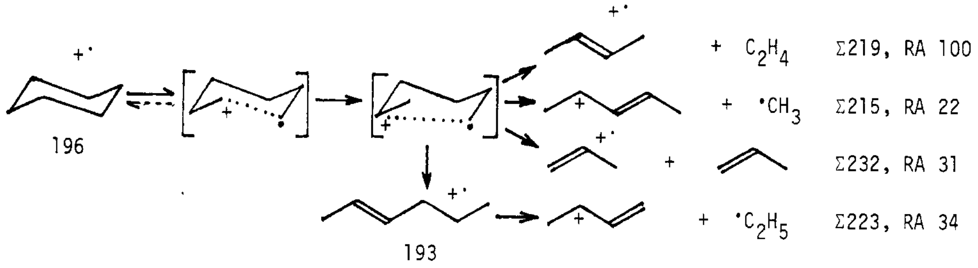
[17] Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 1.

[18] Fuchs, R.; Peacock, L. A. *Can. J. Chem.* **1979**, *57*, 2302.

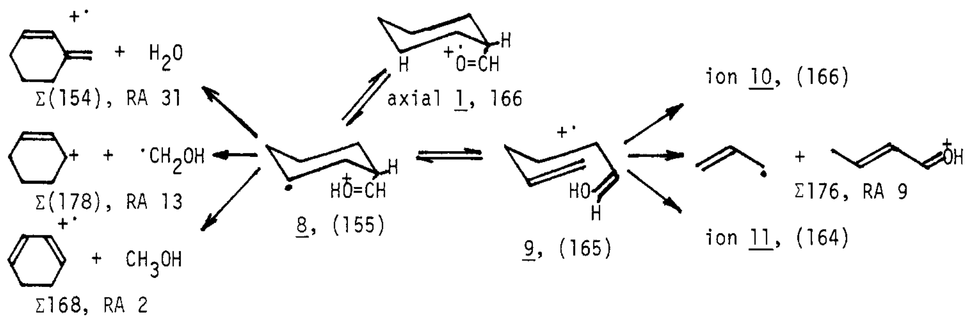
Scheme III



Scheme IV



Scheme V



of the $[M - C_5H_7]^+$ ion (RA = 20) which was the base ion in the mass spectrum of *endo*-**2**. The equivalent ion was the base ion in the mass spectra of both *exo*- and *endo*-methylbicyclo[2.2.1]heptane-2-carboxylate.[22]

Ring bond stretching (see next section) appears to occur in *exo*-$2^{+\cdot}$ before hydrogen abstraction by the oxygen atom because the distance between the oxygen atom and the nearest hydrogen atom is ~2.2 Å, more than the allowable distance of 1.8 Å[11] (Scheme I). With a small geometry change after bond stretching the hydrogen atom on the bridgehead carbon atom could be abstracted by the oxygen atom to give ion **3**. This ion could undergo a simple cleavage to give the $[M - C_5H_7]^+$ ion.

The distance between the oxygen atom and the nearest hydrogen atom in *endo*-**2** is 1.6 Å, within the allowable distance for hydrogen abstraction.[11] The resulting intermediate ion and other rearranged ions of lower energy than the molecular ion are shown in Scheme II. Simple cleavage of two bonds in ion **4** would result in loss of 1-cyclopenten-4-yl which has a ΔH_f 12 kcal/mol greater than the isomeric 1-cyclopenten-3-yl.[4] Thus, the $[M - C_5H_7]^+$ ion apparently is formed via ion **6** as is the $[M - C_2H_4O]^{+\cdot}$ ion, which also occurs in high abundance.

The $[M - H_2O]^{+\cdot}$ ion, which does not occur in the mass spectrum of *exo*-**2**, appears to arise via a complex process. The very low relative abundance (RA = 2) of the molecular ion in *endo*-$2^{+\cdot}$ indicates a process of low E_0 which could be the $[M - H_2O]^{+\cdot}$ process.[23]

There was a moderate amount (RA = 20) of the α-cleavage ion in the mass spectrum of *endo*-**2**.[11] This high-energy process is in competition with the initial hydrogen abstraction process because of its high frequency factor.

Comparison of the mass spectra of these fixed conformers[24] with the mass spectrum of **1** will be made in the discussion of the fragment ions from $1^{+\cdot}$.

Carbon–Carbon Bond Stretching in Molecular Ions. Carbon–carbon bond cleavage reactions in molecular

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(19) Brown, H. C. (with comments by Schleyer, P. v. R.) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

(20) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540.

(21) Attina, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1981**, *103*, 4711.

(22) Eggelte, T. A.; Nibbering, N. M. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 605.

(23) Although several structures are possible for the $[M - H_2O]^{+\cdot}$ ion, 3,5-dimethylene-4-methylcyclohexene cation radical can be formed from ion 4 by cleavage of the bridge bond and two H shifts before loss of H_2O. The estimated energy level for the formation of this ion by using an IE of 8.4 eV for the corresponding neutral molecule, 0.05 eV less than the IE of 2-methyl-1,3-pentadiene,[6] is approximately the same as the ΔH_f of $2^{+\cdot}$. With a third H shift, a more conjugated ion can be formed with a lower energy level.

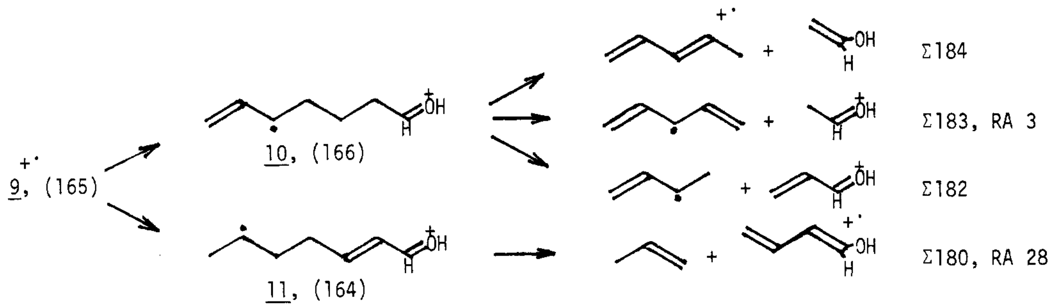
(24) Other fixed conformers related to 1 are *cis*- and *trans*-4-*tert*-butylcyclohexanecarboxaldehyde. The mass spectrum of a mixture of the conformers[25] showed no $[M - CHO]^+$, $[M - H_2O]^{+\cdot}$, or $[M - C_2H_4O]^{+\cdot}$ ions which are characteristic of the mass spectrum of 1. Mass spectra of *cis*- and *trans*-4-*tert*-butylcyclohexanecarboxylic acid[26] also showed no $[M - COOH]^+$ or $[M - C_2H_4O_2]^{+\cdot}$ ions which are characteristic of the mass spectrum of cyclohexanecarboxylic acid.[27] The major difference in the mass spectra of the conformers was the large loss of the *tert*-butyl group (RA = 55) from the trans conformer with almost no loss of this group from the cis conformer.[26] These results indicate that the presence of the *tert*-butyl group dominates the fragmentation pattern so that no comparison can be made with the mass spectra of the nonfixed conformers.

(25) House, H. O.; Lubinkowski, J.; Good, J. J. *J. Org. Chem.* **1975**, *40*, 86.

(26) Van Bekkum, H.; Van de Graaf, B.; Van Minnen-Pathuis, G.; Peters, J. A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 521.

(27) (a) Cornu, A.; Massot, A. "Compilation of Mass Spectral Data"; Heydon and Son: London, 1966. (b) Stenhagen, E.; Abrahamsson, S.; McLafferty, F. "Registry of Mass Spectral Data"; Wiley: New York, 1974. (c) "Eight Peak Index of Mass Spectra", 2nd ed.; Mass Spectrometry Data Center: Aldermaston, UK, 1974. (d) Heller, S. R.; Milne, G. W. "EPA/NIH Mass Spectral Data Base", *Natl. Stand. Ref. Data Ser.*, (*U.S., Natl. Bur. Stand.*) **1978**, NSRDS-NBS-63.

Scheme VI



ions of alkanes have been proposed to occur in the following way[28] (Scheme III). The incipient primary cation resulting from the initial bond-stretching reaction in *n*-butane rearranges irreversibly to a secondary cation in the complex.[28] The ΔH_f of the first intermediate species was shown to be no higher than the calculated and experimental energy level for the $[M - CH_3]^+$ ion and no lower from the similar experimental energy level for the $[M - CH_4]^{+\cdot}$ ion.[28,29] The ΔH_f of the second intermediate species was shown to be 6–7 kcal/mol less than the ΔH_f of the first intermediate species from the lower experimental energy level for the $[M - CH_4]^{+\cdot}$ ion from 2-methylpropane than from *n*-butane.[29]

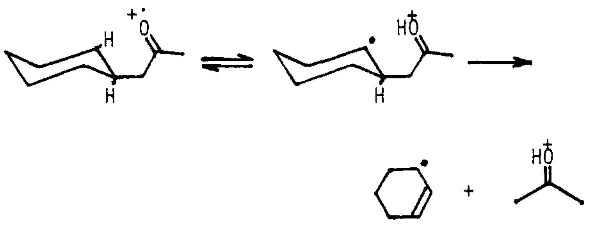
In many examples, the E_0 varied from 5 to 9 kcal/mol for carbon–carbon bond stretching in alkane molecular ions to form an incipient primary cation.[29,32]

Primary Ions from the Cyclohexane Cation Radical. The measured AE's of the ions from the cyclohexane cation radical[33] are consistent with the product-ion energy levels for the structures indicated in Scheme IV. Carbon–carbon bond stretching as in the *n*-butane cation radical (Scheme III) to give the analogous intermediate species (Scheme IV) appears to be involved because each fragment ion and its neutral fragment contain at least two CH_3 groups.

Primary Ions from Axial $1^{+\cdot}$. The conformation of axial $1^{+\cdot}$ is analogous to *endo*-$2^{+\cdot}$ with the hydrogen atom in the 3-position within the allowable distance for hydrogen atom abstraction by the carbonyl oxygen atom. The resulting intermediate ion **8** of lower energy than the molecular ion is shown in Scheme V with further rearrangement and fragmentation processes (Schemes V and VI) to give the *m/z* 94, 81, 80, 71, 70, and 45 ions. In Table I are given the experimental energy levels which are consistent with the fragment ion structures in Schemes V and VI. Of these ions, the *m/z* 94 (RA = 31) and 70 (RA = 28) ions were moderately abundant ions.

The *m/z* 94 ion results from loss of H_2O analogous to the loss of H_2O from *endo*-$2^{+\cdot}$.[11] There was a large metastable ion for this process which is consistent with its low E_0 (Table I). The structure given in Scheme V for the $[M - H_2O]^{+\cdot}$ ion involves the least number of hydrogen shifts compared to alternative ions.

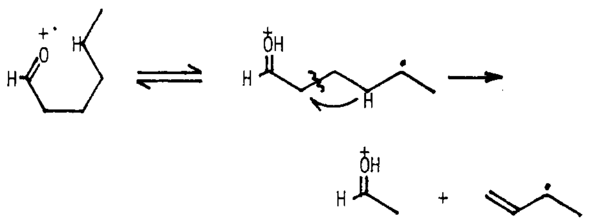
The loss of $\cdot CH_2OH$ (*m/z* 81, RA = 13) occured to a lesser extent in $1^{+\cdot}$ and much less (RA = 4) in *endo*-$^{2+\cdot}$.[11] This process is somewhat similar to the McLafferty +1 fragmentation in cyclohexylacetone (eq 1).[35]



(1)

The formation of the *m/z* 71, 70, and 45 ions involves ring opening after the initial hydrogen-abstraction step as shown in Schemes V and VI. A comparison of the formation of these ions with the other ions from *endo*-$2^{+\cdot}$.[11] indicates few similarities. Intermediate ion **10** (Scheme VI) which is analogous to intermediate ion **6** (Scheme II) appears not to give the $[M - CH_2{=}CHOH]^{+\cdot}$ ion to any extent in $1^{+\cdot}$. (For further discussion, see the section on the $[M - CH_3CHO]^{+\cdot}$ ion from $1^{+\cdot}$.)

The *m/z* 45 ion which occurs in very low abundance in $1^{+\cdot}$ probably is formed from ion **10** by a mechanism similar to the formation of the *m/z* 45 ion from the hexanal cation radical[36] (eq 2).



(2)

The *m/z* 57 ion may be formed from axial $1^{+\cdot}$ via ion **10** by a similar 1,2-elimination (Scheme VI). However, a more direct mechanism is from equatorial $1^{+\cdot}$ (see below) analogous to the mechanism for the formation of the *m/z* 71 ion from *exo*-$2^{+\cdot}$ (Scheme I). The formation of the *m/z* 71 ion from *endo*-$2^{+\cdot}$ involves a facile 1,5-H shift in ion **6** with subsequent cleavage (Scheme II).

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(28) Wendelboe, J. F.; Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 2333.

(29) Steiner, B.; Giese, C. F.; Inghram, M. G. *J. Chem. Phys.* **1961**, *34*, 189. The IE's and AE's reported in this paper were adjusted to an IE of 10.4 eV for 2-methylpropane.[30] The adjusted AE's for the $[M - CH_3]^+$ ion from *n*-butane and 2-methylpropane gave energy levels similar to the calculated energy levels. Using a value for the ΔH_f of $(CH_3)_2CH^+$ obtained in the same laboratory as their AE values, Wolkoff and Holmes[31] concluded that the $[M - CH_3]^+$ process from both *n*-butane and 2-methylpropane proceeded within 0.05 eV of the calculated threshold.

(30) Mead, P. T.; Donchi, K. F.; Traeger, J. C.; Christie, J. R.; Derrick, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3364.

(31) Wolkoff, P.; Holmes, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 7346.

(32) (a) Wendelboe, J. F.; Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1981**, 958. (b) The E_0 of 6 kcal/mol for the formation of the $[M - C_2H_5]^+$ and $[M - C_2H_6]^{+\cdot}$ ions from 2-methylpentane$^{+\cdot}$[29] represents the E_0 for the bond stretching reaction because the calculated E_0 for the formation of these ions is ~0.

(33) Sergeev, Y. L.; Akopyan, M. E.; Vilesov, F. I.; Chizhov, Y. V. *Khim. Vys. Energ.* **1973**, *7*, 418. The *m/z* 83 and 43 ions are not included because of a lower RA and a higher AE than the ions shown in Scheme IV. The $[M - CH_3]^+$ ion is shown as having the structure given in Scheme IV because the $[M - CH_3]^+$ ion from the methylcyclopentane cation radical was shown to be ~50% the ring-opened ion.[34] The structure of the acyclic C_5H_9 ion from bromocyclopentane was consistent with the protonated 1,3-pentadiene structure.[20]

(34) Bursey, J. T.; Bursey, M. M.; Kingston, D. G. I. *Chem. Rev.* **1973**, *73*, 191.

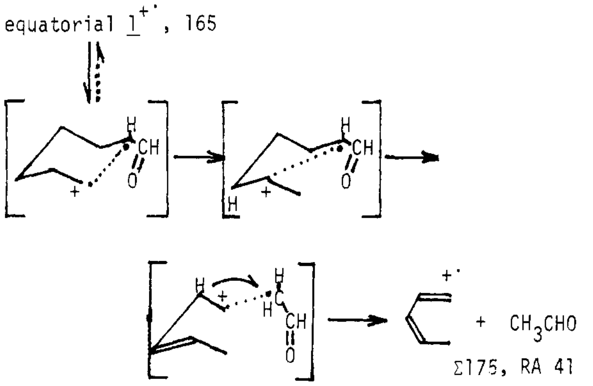
(35) Eadon, G. *Org. Mass Spectrom.* **1977**, *12*, 671.

(36) Derrick, P. J.; Falick, A. M.; Lewis, S.; Burlingame, A. L. *J. Phys. Chem.* **1979**, *83*, 1567.

The loss of $\cdot C_3H_5$ from *endo*-$2^{+\cdot}$ (Scheme II) is not analogous to the loss of $\cdot C_3H_5$ from axial $1^{+\cdot}$ (Scheme V). However, it is somewhat analogous to the loss of C_3H_6 from axial $1^{+\cdot}$ in that intermediate ion 11 (Scheme VI) is analogous to intermediate ion 7 (Scheme II). Simple cleavage of ion 11 gives the $[M - C_3H_6]^{+\cdot}$ ion.

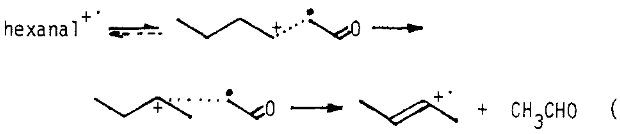
Loss of CH_3CHO from $1^{+\cdot}$. In estimating the energy levels (Table I) for the m/z 68 ion, assuming loss of $CH_2{=}CHOH$, and the m/z 70 ion, the same additivity values were used so that the uncertainty in these values would not be a factor in comparing the two energy levels. The IE of 1,3-pentadiene (8.6 eV[37]) is higher than the IE of 1-hydroxy-1,3-butadiene (8.4 eV[38]). Thus, the estimated energy level for the m/z 68 ion, assuming loss of $CH_2{=}CHOH$, is higher than that for the m/z 70 ion by the difference in the IE's of the corresponding molecules. Experimentally this is not the case. The parallel semilogarithmic curves for the m/z 68 and 70 ions indicated an AE for the m/z 68 ion 0.2 eV lower than that for the m/z 70 ion, consistent with the loss of CH_3CHO instead of $CH_2{=}CHOH$ (Table I).

The loss of CH_3CHO appears to arise from equatorial $1^{+\cdot}$ because it does not involve a hydrogen transfer to the oxygen atom. The formation of this ion as shown in eq 3 involves the stretching of the β bond to the carbonyl group as in cyclohexane (Scheme IV). The other β bond may also be weakened, resulting in the third intermediate species. The $[M - CH_3CHO]^{+\cdot}$ ion is the most abundant ion at 50 eV, involving rearrangement, and so indicates a relatively high frequency factor for the process.



(3)

The loss of CH_3CHO has been proposed to occur in the mass spectrum of hexanal.[39] A mechanism similar to the loss of CH_4 in n-butane (Scheme III) would give the $[M - CH_3CHO]^{+\cdot}$ ion (eq 4).



(4)

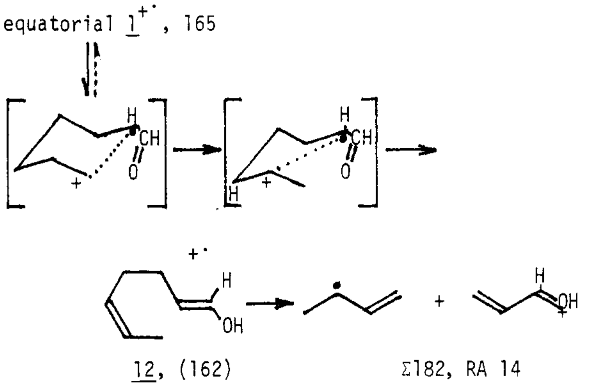
Other Primary Ions from Equatorial $1^{+\cdot}$. Stretching of the ring bond in equatorial $1^{+\cdot}$ as in eq 3 may lead to the m/z 84 ($[M - C_2H_4]^{+\cdot}$, RA = 6) and 56 (RA = 10) ions analogous to the formation of the m/z 56 ion from the cyclohexane cation radical (Scheme IV). A small metastable ion was observed for the m/z 84 process. The $[M - CH_3]^+$ ion also occurs in the mass spectrum of cyclohexane and occurs in low relative abundance (RA = 5) in the mass spectrum of 1.

Table II. Abundances of the Ions from $1^{+\cdot}$ at Low Voltages

	abundance,[a] %			
m/z	9.5 eV[b]	10 eV[b]	10.5 eV[b]	11.0 eV[b]
112	10	61	238	585
94	6	41	185	480
68		7	42	180
70			10	49
71			9	39
83			6	41
97			5	21
82				2
45				4
81				6
56				6
57				8
% equatorial[c]	62	62	59	59

[a] Corrected for isotope abundance. [b] Nominal voltage. [c] Sum of abundances of m/z 112, 68, 83, 97, 82, 56 and 57 as the percent of abundances of all the ions listed.

The formation of the m/z 57 ion (RA = 14) from equatorial $1^{+\cdot}$ as shown in eq 5 also involves bond stretching as in eq 3. In this case, after the formation of the second intermediate species in the complex and with a small change in geometry, the equatorial carbonyl oxygen atom is in position[40] to abstract the 4-hydrogen atom. Simple cleavage of the resulting intermediate cation gives the m/z 57 ion. This process is analogous to the formation of the m/z 71 ion from *exo*-$2^{+\cdot}$ (Scheme I).



(5)

The α-cleavage process to give the m/z 83 ion is the major process in $1^{+\cdot}$ and may be from both conformers as in *exo*- and *endo*-$2^{+\cdot}$.[11] There was a small amount of the m/z 82 ion (RA = 4) involving the loss of H_2CO.

Comparison of Ion Abundances from Each Conformer at Different Voltages. In Table II are given the ion abundances from $1^{+\cdot}$ at various low voltages and the percent of the ion abundances attributed to equatorial $1^{+\cdot}$. Included in this figure is all of the molecular ion abundance. The decrease in this percent from 9.5 to 11 eV is indicative of a small amount of the molecular ion abundance due to axial $1^{+\cdot}$. This low abundance is consistent with the E_0 of 0.1 eV for the $[M - H_2O]^{+\cdot}$ ion from axial $1^{+\cdot}$ and with the low abundance (RA = 2) of the molecular ion from *endo*-$2^{+\cdot}$[11] in which the $[M - H_2O]^{+\cdot}$ ion presumably has the lowest E_0.[23] A higher molecular ion abundance from equatorial $1^{+\cdot}$ is consistent with the higher E_0 (0.6 eV) for the m/z 68 ion which has the lowest E_0 of the ions attributed to equatorial $1^{+\cdot}$.

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(37) Bees, M.; Bieri, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028.

(38) Terlouw, J. K.; Heerma, W.; Holmes, J. L.; Burgers, P. C. *Org. Mass Spectrom.* **1980**, *15*, 582.

(39) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.

(40) The stable rotamer of equatorial 1 is as shown in eq 3. See: Karabatsos, G. J.; Hsi, N. *J. Am. Chem. Soc.* **1965**, *87*, 2864. Kao, P. N.; Turner, P. H. *Ibid.* **1979**, *101*, 4497.

At 50 eV, the percent of the ion abundances (including secondary ions, Experimental Section) attributed to equatorial $1^{+\cdot}$ is ~71%. This percent includes RA = 26 for the molecular ion and all of the α-cleavage ion abundance. The RA = 2 for the molecular ion attributed to axial $1^{+\cdot}$ is similar to the molecular ion abundance from *endo*-$2^{+\cdot}$.[11] However, part of the α-cleavage ion abundance could be due to axial $1^{+\cdot}$ because the α-cleavage ion from *endo*-$2^{+\cdot}$ is moderately abundant (RA = 20).[11] A 25% α-cleavage ion abundance (including secondary ions) from axial $1^{+\cdot}$ at 50 eV is consistent with an equatorial/axial proportion of 60:40, similar to the proportion at low voltages.

The equatorial conformation of 1 is more stable than the axial conformation.[41] At 150 °C, the ion-source temperature, the equilibrium conformation of 1 was calculated to be 68% equatorial and 32% axial from the temperature dependence of the equilibrium at low temperatures in CD_2Cl_2.[41] In the gas phase, the percent of equatorial conformer may be less because many solvents are known to cause an increase in the percent of the more stable conformer.[42]

Conclusions

The data presented suggest that the axial and equatorial conformers of $1^{+\cdot}$ fragment with little interconversion before fragmentation. Bond stretching of the equatorial ring bond (eq 3) appears to occur at a faster rate than conversion to the axial conformer. This is reasonable because the E_0 for bond stretching in alkane molecular ions has been shown to be 5–9 kcal/mol[28,29,32] which is lower than the barrier of ~11 kcal/mol for interconversion of the radical cations of cyclohexyl conformers if similar to the barrier in neutral cyclohexane derivatives.[3] In addition, the high abundance of the $[M - CH_3CHO]^{+\cdot}$ ion at 50 eV (Table I) indicates a relatively high frequency factor for the bond-stretching process. In the axial conformer of $1^{+\cdot}$ hydrogen abstraction by the oxygen atom is geometrically favorable and is a lower energy process than ring bond stretching.

Experimental Section

The 50-eV mass spectrum of 1 was determined on a Du Pont 21-491/492 mass spectrometer with a 2-kV ion accelerating voltage and a 150 °C ion-source temperature. The primary ions and relative abundances are given in Table I. Secondary ions from $1^{+\cdot}$ which are not given in Table I are as follows: *m/z* (relative intensity) 79 (24), 77 (4), 69 (9), 67 (14), 66 (7), 55 (100), 53 (8), 43 (7), 41 (42), 39 (20). For the estimation of the percent of the ion abundances at 50 eV due to the equatorial conformer, the abundances of the following secondary ions were attributed to the equatorial conformer: *m/z* 67, 55, 41, 39.

High-resolution measurements (CEC 21-110 mass spectrometer) on *m/z* 84, 83, 82, 81, 80, 79 (C_6H_7), 71, 70, 68, 57, and 56 from $1^{+\cdot}$ indicated the empirical structures given for the ions in Table I. Metastable ions were observed for the following primary and secondary processes in $1^{+\cdot}$ (given as *m/z* values): 112 → 94, 112 → 84, 94 → 79, 83 → 55, 82 → 67.

The ionization energy of 1 and the AE's of its primary fragment ions as given in Table I were determined by the semilogarithmic method[43] from data obtained on a Du Pont 21-491/492 double-focussing mass spectrometer at a low repeller voltage, an ion-accelerating voltage of 2 kV, and an ion-source temperature 150 °C. Acetone was used as the internal standard: IE, 9.7 eV; AE (*m/z* 43), 10.3 eV.[8]

Appearance energy measurements by the semilogarithmic method have been considered to be inaccurate in an unpredictable manner.[7c] Our experience has been that the position of the curves on the log I/I_{50} scale varies according to instrumental factors. It is well-known that the position of the curves on the electron volt scale varies.[7c] Thus, measuring the AE values at I/I_{50} = 0.001 gives different values depending on the instrumental factors. By use of an internal standard with a fragment ion of known AE, the I/I_{50} value can be determined, which gives the correct AE for the fragment ion of the internal standard. This I/I_{50} value is then used to determine the AE's of the ions for the compound being measured. This I/I_{50} value is less than 0.001 and involves some extension of the curves beyond the measured points. Only the most abundant ions at 50 eV could be detected below the I/I_{50} = 0.001 level. Focussing at low voltages was necessary.

The IE of 1 was determined to be 9.6 eV; the AE's for the *m/z* 94, 68, 70, and 83 ions were found to be 9.7, 10.0, 10.2, and 10.4 eV, respectively. The curves for these ions were approximately parallel so that the AE differences between the ions should be semiquantitatively correct.[7a]

The AE's for the other ions given in Table I were less accurate because of the low abundance of the ions. The curves for the *m/z* 71 and 97 ions were nearly the same as for the *m/z* 68 ion, and thus the AE's for these ions were estimated to be 10.0 eV. The curves for the *m/z* 45, 57, 81, and 82 ions were similar to the curve for the *m/z* 83 ion. The AE's for these ions were estimated to be 10.4 eV. The curve for the *m/z* 56 ion indicated an AE of 10.5 eV, 0.1 eV greater than that for the *m/z* 83 ion. The AE's for the *m/z* 56 and 57 ions in relation to the AE for the *m/z* 83 ion were more accurate from data taken without acetone as an internal standard.

Cyclohexanecarboxaldehyde was purchased from the Aldrich Chemical Co. (purity 98%). The mass spectrum was similar to the reported mass spectrum[27] except for the peaks due to the cyclohexanecarboxylic acid impurity in the reported spectrum.[27d]

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Appendix

The majority of the ΔH_f's of the neutral molecules in Table I, the schemes, and the equations were from experimental values[4,44-46] or estimated from the group additivity procedure.[4] The ΔH_f of $\cdot CH_3$[47] was a value recently determined. The ΔH_f of $(CH_2{=}CH)_2CH\cdot$ was from a recent compilation.[44] The ΔH_f of $\cdot CH_2OH$ was calculated from the bond-dissocation energy (BDE) of 94 kcal/mol for $H{-}CH_2OH$,[48] that of $CH_3\dot{C}HCHO$ from the BDE of 91.2 kcal/mol for the α-CH bond of propanal,[49] and that of $CH_2{=}CH\dot{C}HOH$ from an estimated BDE of 81 kcal/mol for the C–H bond in $CH_2{=}CHCH_2OH$, slightly less than the BDE of 82.5 kcal/mol for the C–H bond in $CH_2{=}CHCH_2CH_3$.[44] From these ΔH_f's the following group additivity values (kcal/mol) were derived: $\cdot C{-}(C)(H)(CO)$, 32.8; $\cdot C{-}(C_d)(H)(O)$, 22.4. The value of −3.1 kcal/mol for $C{-}(H)(C)_2(CO)$ was derived from the ΔH_f of −52.1 kcal/mol for 2-methylpropanal.[50] The value of −46.2 kcal/mol for

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(41) Buchanan, G. W.; McCarville, A. R. *Can. J. Chem.* **1972**, *50*, 1965.

(42) Ramos, J. J. M.; Dumont, L.; Stien, M. L.; Reisse, J. *J. Am. Chem. Soc.* **1980**, *102*, 4150.

(43) (a) Lossing, F. P.; Tickner, A. W.; Bryce, W. A. *J. Chem. Phys.* **1951**, *19*, 1254. (b) Dibeler, V. H.; Reese, R. M. *J. Res. Natl. Bur. Stand. (U.S.)* **1955**, *54*, 127.

(44) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

(45) Stull, D. R.; Westrum, E. F.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

(46) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(47) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 3214.

(48) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(49) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

$O{-}(H)(C_d)$ was derived from the ΔH_f of −39.7 kcal/mol for the enol of acetone.[51]

The ring correction value for a radical which is part of a ring was taken to be the average of the saturated and unsaturated ring correction values.[4] The ring correction values for norbornene and norbornane were calculated from their ΔH_f's[15] to be 21.9 and 15.9 kcal/mol, respectively. The ring correction value of 1.6 kcal/mol for the exocyclic double bond was derived from the ΔH_f of methylenecyclohexane.[18] The ΔH_f of *endo*-**2** was estimated to be 1 kcal/mol greater than that of *exo*-**2**.[19]

The IE's of the radicals were derived or extrapolated from experimental ΔH_f's of cations which in most cases were determined from proton affinity (PA) values.[17] A comprehensive PA scale[17] was based on a ΔH_f of 166 kcal/mol for the *tert*-butyl cation and a ΔH_f of 367.2 kcal/mol for the H^+ ion. However, the ΔH_f of the *tert*-butyl cation was recently determined to be 162.1 kcal/mol from the photoionization AE of the $[M - H]^+$ ion from isobutane.[14] Thus, many of the ΔH_f values used in this study were based on the comprehensive PA scale[17] adjusted to a ΔH_f of 162.1 kcal/mol for the *tert*-butyl cation.[14] The ΔH_f of the α-cleavage ion from *exo*- and *endo*-$\mathbf{2}^{+\cdot}$ was derived from the ΔH_f of the 2-norbornyl cation.[12]

Vajda and Harrison[52] have measured the PA's of propenal and 2-butenal relative to standards. After adjustment to the revised PA scale of Aue and Bowers[17] the PA's of propenal and 2-butenal were found to be 197.3 and 204.3 kcal/mol, respectively. For calculation of the ΔH_f of the cations, accurate values for the ΔH_f of propenal and 2-butenal were needed. The ΔH_f(liquid) of 2-butenal, −34.45 kcal/mol[45], and the ΔH_{vap} of butanal, 8.05 kcal/mol, were considered to be good values.[45,46] The ΔH_{vap} of methyl and ethyl acrylates is 0.2 kcal/mol less than the ΔH_{vap} of the corresponding saturated compounds,[53] and the ΔH_{vap} of propenal[53] is 0.2 kcal/mol less than the ΔH_{vap} of propanal.[45,46] Thus, the ΔH_{vap} of 2-butenal was estimated to be 7.85 kcal/mol, 0.2 kcal/mol less than the ΔH_{vap} of butanal, giving a value for the ΔH_f(2-butenal) of −26.6 kcal/mol. There was no good value for the ΔH_f(liquid) of propenal. However, by Benson's additivity method[4] the ΔH_f of propenal should be 7.8 kcal/mol greater than the ΔH_f of 2-butenal, giving a value of −18.8 kcal/mol for the ΔH_f of propenal. The additivity value for $C_d{-}(H)(CO)$ thus would be 4.0 kcal/mol instead of 5.0 kcal/mol.[4] The ΔH_f of $H_2C{=}CHCHOH^+$ and $CH_3CH{=}CHCHOH^+$ and the IE's of the corresponding radicals were then calculated to be 151.1 and 136.3 kcal/mol and 6.6 and 6.3 eV, respectively. The IE for the radical corresponding to the $[M - C_3H_5]^+$ ion in Scheme II was estimated to be 6.1 eV, 0.2 eV less than the IE of $CH_3CH{=}CH\dot{C}HOH$.

The adjusted PA's of cyclopentadiene, 1,3-pentadiene, and 2-methyl-1,3-butadiene[17] give the following ΔH_f's (kcal/mol) of the cations and IE's (eV) of the corresponding radicals: $\overline{\mathrm{CH_2CH{=}CHC^+HC}}\mathrm{H_2}$, 195.2, 6.8; $CH_3CH{=}CHC^+HCH_3$, 179.6, 6.85; $CH_2{=}CHC^+(CH_3)_2$, 181.0, 7.0. These IE's are 0.2 eV lower than the IE's measured for these radicals.[6,54] Thus, the IE for $CH_2{=}CH\dot{C}HCH{=}CH_2$ was estimated to be 7.05 eV, 0.2 eV less than the measured value.[6]

The PA's of propene, cyclopentene, and cyclohexene gave ΔH_f's of the corresponding cations as 184.5 ± 2.1, 183.8 ± 1.9, and 171 ± 3 kcal/mol, respectively, relative to the ΔH_f of 162.1 kcal/mol for the *tert*-butyl cation.[20] From these ΔH_f's the IE's of the corresponding radicals were calculated: $CH_3\dot{C}HCH_3$, 7.25 eV; $\overline{\mathrm{CH_2(CH_2)_2\dot{C}HC}}\mathrm{H_2}$, 6.95 eV; $\overline{\mathrm{CH_2(CH_2)_3\dot{C}HC}}\mathrm{H_2}$, 6.85 eV.

The IE of 1-ethyl-1,3-cyclopentadiene was estimated to be 8.2 eV.[55] Literature values were used for the IE's of propene (9.7 eV[56]), 2-butene (9.1 eV[56]), 2-hexene (8.9 eV[6]), and cyclohexane (9.8 eV[56]).

Estimated IE's of the neutral molecules, radicals, and biradicals corresponding to the ions in the schemes and equations are given as follows, with two of the reference IE's from the PA scale[17] adjusted to the ΔH_f of 162.1 kcal/mol for the *tert*-butyl cation:[14] **2**, 9.5 eV, 0.1 eV less than the IE of **1**;[57] **3**, 8.4 eV, same as the IE of $C_2H_5CH{=}CHOH$;[59] **4**, 6.3 eV, same as the IE of $(CH_3)_2CH\dot{C}HOH$;[17] **5**, see ion **3**; **6**, 6.4 eV, same as the IE of $CH_3(CH_2)_3\dot{C}HOH$;[17] **7**, 6.3 eV, same as the IE of $CH_3CH{=}CH\dot{C}HOH$ (see above); **8**, see ion **4**; **9**, see ion **3**; **10**, see ion **6**; **11**, see ion **7**; **12**, see ion **3**.

Registry No. Cyclohexanecarboxaldehyde, 2043-61-0.

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